COMBINED LIQUID CHROMATOGRAPHY/STABILITY TESTING (LC/ST) APPROACH FOR ISOLATION OF COMPOUNDS RESPONSIBLE FOR FUEL INSTABILITY

By

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INTRODUCTION

The bulk of prior work on fuel stability problems indicates that the instability of a given fuel usually can be attributed to a relatively small subset of compounds/compound types which are typically present at low abundance in the fuel. For example, recent work has implicated alkylindoles, alkylphenalenes, and sulfonic acids as major contributors to storage instability of diesel fuel (1-12). Phenolic compounds also contribute to diesel sediment formation (13,14), and carboxylic or other acids of similar or greater acidity accelerate the rate of sediment formation (15).

Sediments formed during storage of jet fuels produced by hydrocracking processes largely contained aromatic hydrocarbons and oxygen-containing compounds (16). In the case of thermal instability of jet fuels, compounds that are either easily converted to peroxyl radicals or hydroperoxides, or are important in propagation of the free radical reactions, are of greatest concern (10). Analysis of JFTOT tube deposits and those on filters downstream of the JFTOT tube has indicated contributions from a wider variety of compound types, relative to those formed in storage sediments (17,18).

A common feature of each type of stability problem cited above is the prominent role played by acidic compounds, either as catalysts or direct participants in sediment/deposit formation. Alkylindoles, sulfonic acids, phenolic compounds, carboxylic acids and hydroperoxides all exhibit acidic (hydrogen donor) properties. As a general correlation, Clark and Smith found that total acid content, as determined by yield of acids from nonaqueous ion exchange liquid chromatography, was the best available predictor of thermal stability (19).

Even where the components responsible for stability problems have been identified, there frequently are many unanswered questions concerning the nature of their interaction to form deposits/sediments, which compounds actually initiate or limit the sediment-forming process, and what reactions control the overall rate of sediment formation. Design of cost-effective methods or approaches to resolve a given stability problem normally requires at least some information concerning the sediment-forming process. For example, the effectiveness of tertiary amine additives in storage stabilization of diesel fuels containing light cycle oil may be attributed to their neutralization of acids which catalyze reactions resulting in gums and sediment (11,15).

Chemical separations have been shown to be an effective means for isolation of components that promote instability, as well as aiding in the determination of relevant reactions leading to deposit/sediment formation (e.g., 2,7,13,14). However, the availability of a general scheme for systematic separation of compound classes in jet or diesel fuels, plus a means for rapidly assessing the impact of the resulting fractions on stability, would further improve the applicability of this approach to fuel stability studies. This report describes a series of liquid chromatographic (LC) separations and reblending/stability testing techniques aimed at meeting this need. Representative results are provided to illustrate the merit of this approach as well as problems encountered in its use. In agreement with work cited above, acidic components are frequently implicated as primary promoters of instability from the results reported herein.

EXPERIMENTAL

Figure 1 outlines the complete sequence of available separations. Procedures for each separation step are described in detail elsewhere (20). Typically, stability testing (Figure 2) is performed after each stage of separation, and those results determine the extent and emphasis of additional separations. For example, further separations of neutrals into subtypes indicated in Figure 1 are not performed unless stability tests indicate significant deposit/sediment formation for the whole neutral fraction. Subfractionation of whole acids and bases is more commonly performed since stability tests on acid + neutral or base + neutral blends frequently implicate one or both of those types as promoters/causes of instability. As noted in Figure 2, whole neutrals are typically used as the blend stock for acid/base fractions or subfractions. Fractions are usually reblended according to their proportions in the whole fuel. Comprehensive recomposites (e.g., acids + bases + neutrals) are tested at each stage of the work to check for bias in stability tests and/or contamination/losses during separations. Details of the storage (typically 2 weeks at 80° C) and thermal (modified D 3241) stability test procedures appear elsewhere (17,21,22).
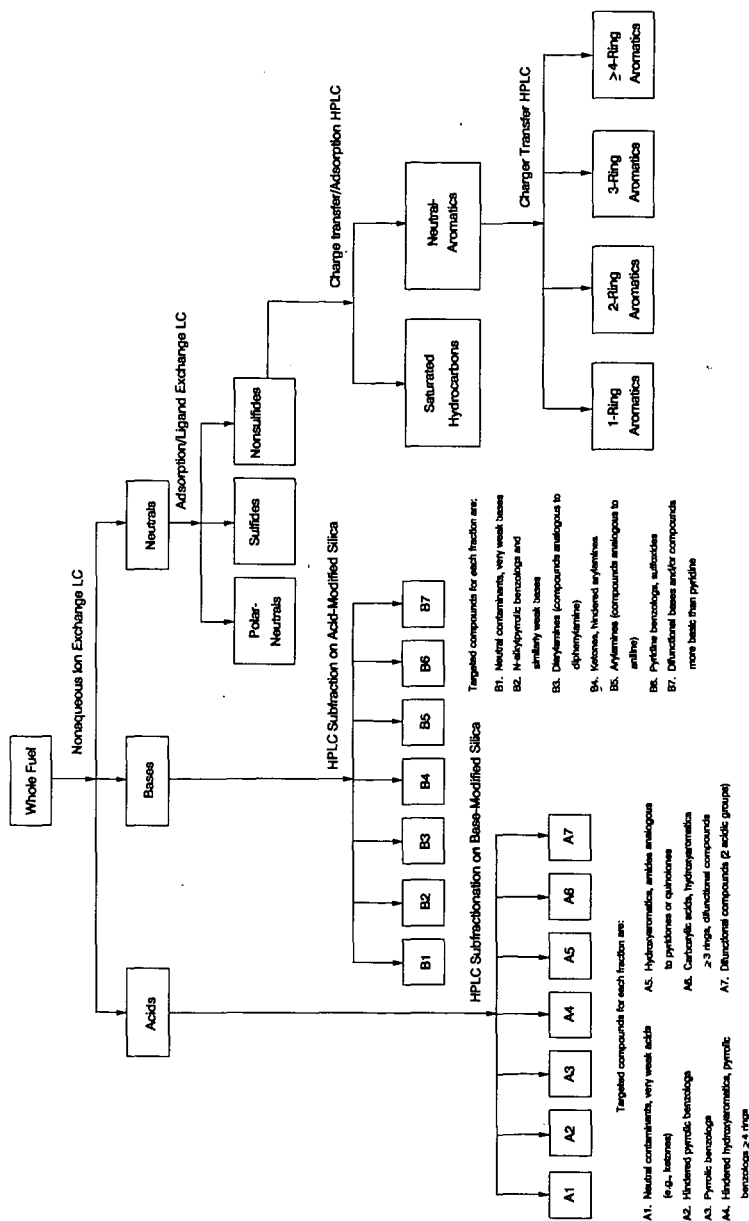
Whole Fuel

Nonaqueous Ion Exchange LC

Acids | Bases | Neutrals

Adsorption/Ligand Exchange LC

Polar-Neutrals | Sulfides | Nonsulfides

Charge transfer/Adsorption HPLC

Saturated Hydrocarbons | Neutral-Aromatics

Charger Transfer HPLC

1-Ring Aromatics | 2-Ring Aromatics | 3-Ring Aromatics | ≥4-Ring Aromatics

HPLC Subfractionation on Base-Modified Silica

A1 | A2 | A3 | A4 | A5 | A6 | A7

Targeted compounds for each fraction are:

A1. Neutral contaminants, very weak acids (e.g., ketones)
A2. Hindered pyrrolic benzologs
A3. Pyrrolic benzologs
A4. Hindered hydroxyaromatics, pyrrolic benzologs ≥4 rings
A5. Hydroxyaromatics, amides analogous to pyridones or quinolones
A6. Carboxylic acids, hydroxyaromatics ≥3 rings, difunctional compounds
A7. Difunctional compounds (2 acidic groups)

HPLC Subtraction on Acid-Modified Silica

B1 | B2 | B3 | B4 | B5 | B6 | B7

Targeted compounds for each fraction are:

B1. Neutral contaminants, very weak bases
B2. N-alkylpyrrolic benzologs and similarly weak bases
B3. Diarylamines (compounds analogous to diphenylamine)
B4. Ketones, hindered arylamines
B5. Arylamines (compounds analogous to aniline)
B6. Pyridine benzologs, sulfoxides
B7. Difunctional bases and/or compounds more basic than pyridine

Figure 1. Schematic for LC Separations. Note that subfractionation of neutrals(i.e. Into Polar-neutrals, sulfides, etc.) is not normally necessary, since neutrals are usually quite stable.
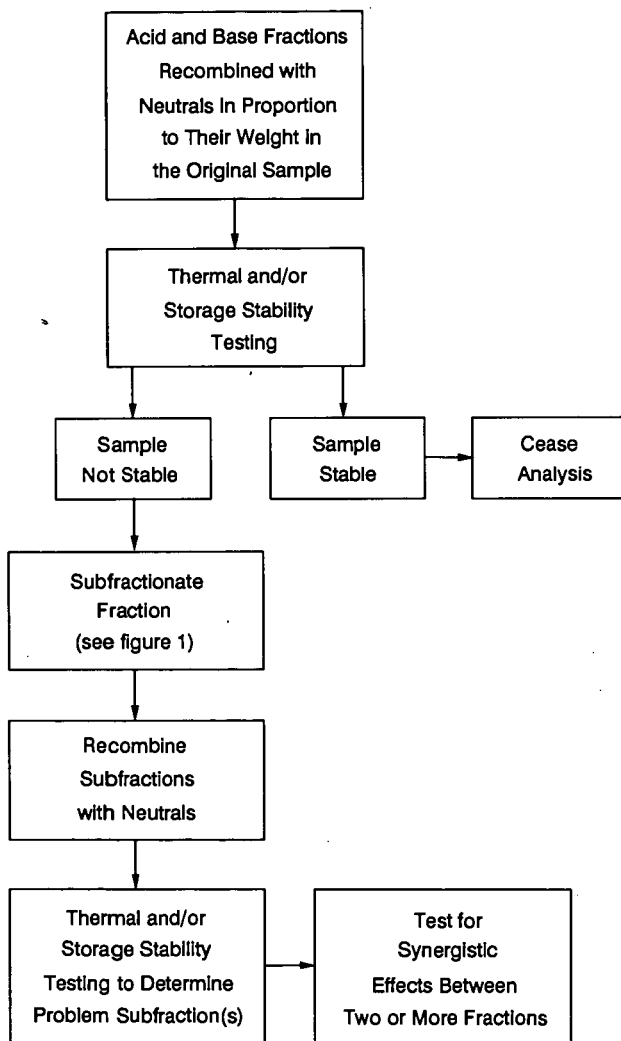
Figure 2. Typical Sequence for Reblending and Stability Testing of Acid and Base Fractions

RESULTS AND DISCUSSION

Tables 1 and 2 show comparisons of thermal stability of two jet fuels (NIPER sample Nos. 2140 and 2302) versus their neutral fractions under mild (Table 1) and moderate (Table 2) thermal stress conditions. The significantly greater thermal stability of neutrals relative to the whole fuel is quite evident from this data. Fraction yields (wt %) from separation of 2140 and 2302 fuels into acids, bases, and neutrals (ABN) were, respectively: 0.17(A), 0.08(B), 98.0(N) (98.2 total); 0.19(A), 0.04(B), 94.5(N) (94.6 total). Thus, removal of a relatively small proportion of acidic/basic material (ca. 0.25 wt %) greatly improved the thermal stability of these two fuels.

TABLE 1
Thermal Stability of Whole Jet Fuels vs. Neutral Fractions,
Standard JFTOT (2½ hrs. @ 260° C)

Sample No.	Fraction	Tube Rating	Pressure Drop (psi)
2140	Whole	4	0
2140	Neutral	1	0
2302	Whole	3	0
2302	Neutral	1	0

TABLE 2
Thermal Stability of Whole Jet Fuels vs. Neutral Fractions,
Extended JFTOT (277° C)

Sample No.	Fraction	Run Time	Tube Deposit Rating	Filter Pressure Drop (psi)
2140	Whole	12 hours	>>4 (black)	filter plugged
2140	Neutral	12 hours	2	0
2302	Whole	3.5 hours	>4 (brown)	filter plugged
2302	Neutral	3.5 hours	1	0

An earlier report discussed mass spectrometric (MS) analysis of JFTOT tube deposits and sediments from downstream filters from both the 2140 and 2302 fuels (17). Those results indicated a predominance of polar compounds in each case, especially when the MS sample introduction probe was heated above 150° C. Components vaporized at temperatures ≥150° C were probably covalently bonded within the sediment structure (17). Thus, the observed improvement in thermal stability of neutrals versus whole fuels is consistent with the lower thermal stability of acidic and basic components indicated by MS analysis.

Because of the relatively large quantities of sample (ca. 500 mL) required by the JFTOT test, differential scanning calorimetry is currently being explored as an alternate means for evaluating the thermal stability of whole acid and base fractions and subfractions thereof. Those results will be reported in a later paper.

Tables 3 and 4 show separation and storage stability test results for a straight-run middle distillate (450-650° F, 0.5 wt % S, 34 °API). Although as a whole the results clearly show acidic types to be largely responsible for sediment formation in this case, close inspection of the data reveals some inconsistencies. The most significant discrepancy is the difference between total sediment for reblended acids + bases + neutrals versus the original distillate (22 versus 8.7 mg/100 mL). The main reason for the higher apparent sediment yield from the reblended sample was found to be incomplete dissolution of the acid fraction into neutrals during the reblending step. The insoluble material in the acid fraction temporarily suspended into the neutrals (giving the appearance of dissolution), but ultimately added to the weight of insolubles obtained by filtration at the end of the stability test. This error is similarly reflected in the high apparent sediment yield for the acids + neutrals blend (21 mg/100 mL).

TABLE 3
Mass Balances from Separation of a North American
Straight-Run Middle Distillate

Fraction[1]	Yield (wt %)
Acids	0.47
A1	0.056
A2	0.019
A3	0.18
A4	0.036
A5	0.047
A6	0.063
A7	0.011
Total, A1-A7	0.412
Bases	0.17
B1	0.082
B2	0.001
B3	0.014
B4	0.013
B5	0.012
B6	0.036
B7	0.018
Total, B1-B7	0.176
Neutrals	98.1
Total, Acids + Bases + Neutrals	98.7

[1]See Figure 1.

TABLE 4

Storage Stability Test Results on Fractions Listed in Table 3[1]

Fraction	Total Sediment (mg/100 mL)	Net Sediment[2] (mg/100 mL)
Acids	21	19
A1	2.7	0.5
A2	8.7	6.5
A3	2.1	-0.1
A4	2.2	0.0
A5	2.2	0.0
A6	7.0	4.8
A7	5.6	3.4
Total, A1-A7	-	15.1
Bases	2.9	0.7
B1	1.9	-0.3
B2	1.4	-0.8
B3	1.5	-0.7
B4	0.7	-1.5
B5	0.5	-1.7
B6	3.4	1.2
B7	5.9	3.7
Total, 81-B7	-	-0.1
Neutrals	2.2	-
Neutrals + Acids + Bases	22	20
Whole Distillate	8.7	-

[1]80° C, 2 weeks, air at ambient pressure. Average of duplicate determinations is shown.

[2]Net sediment = total sediment - sediment from neutrals. (Neutrals were used as diluent for all acid and base fractions).

Because of the unreliability of simple visual inspection of reblended samples for assessment of solubility, they are now routinely prefiltered prior to stability testing. This precaution has significantly improved balances in stability test results for composited fractions versus whole materials over those obtained in early work such as that illustrated in Table 4. The source of the insoluble material is not well defined; contributions from solvent impurities and materials used in the separations (e.g., ion exchange resin artifacts) are suspected. In addition, degraded or otherwise altered fuel components probably make up part of the insoluble material in many cases. It should be emphasized that the overall magnitude of insolubles is quite small. For example, the acid fraction comprises 0.47 wt % (equivalent to ca. 425 mg/100 mL) of the middle distillate; the portion that did not dissolve (ca. 13 mg/100 mL) amounted to only about 3 percent of the acid fraction.

For the purpose of determining sediment directly attributable to a given acid or base fraction, the sediment formed by neutrals alone is typically subtracted from the total sediment for a given acid/base + neutrals blend (see "net sediment" data, Table 4). Although sediment formation may not be strictly an additive property, this or a similar practice is necessary to derive balances for sediment formation of individual fractions for comparison with the whole. Otherwise, the sediment contribution from the neutral fraction would be propagated in proportion to the number of fractions tested, and balances over fractions would invariably exceed that of the whole.

In light of the above discussion, it may be seen that most base sub-fractions from the middle distillate apparently stabilize the neutral fraction (B1-B5), and only two (B6 and B7) provide a positive net sediment yield. The balance for net sediment yield calculated over the base subfractions (-0.1 mg/100 mL) is within experimental error of that determined for the whole bases (0.7 mg/100 mL). In the case of the acid subfractions, the apparent sediment yield for A2 (6.5 mg/100 mL) is believed to have resulted largely from incomplete solution rather than actual sediment formation. Thus, the dominant sediment-forming acidic compounds are present in A6 and A7, which provide a combined sediment yield (8.2 mg/mL) consistent with that of the whole distillate (8.7 mg/mL). Thus, in the case of both acids and bases, compounds exhibiting the highest polarity/degree of functionality in terms of separation behavior (see the description of subfractions B6, B7, A6, and A7 composition in Figure 1) also show the highest sediment-forming tendency. Their combined concentration in the distillate is extremely low, ca. 0.1 wt %. Effective removal or neutralization of the effects of these compounds should improve the storage stability of the distillate to the level of sediment formation exhibited by the neutral fraction (2.2 mg/100 mL).

CONCLUSIONS

The combination of LC separation and stability testing (LC/ST) is an effective screening tool for identifying components/compound types that promote instability. The LC fractions also constitute a valuable resource for studying sediment formation pathways, synergistic effects between different compound types, and the effectiveness of potential stabilizing additives.

The sensitivity of stability tests to contamination and sample alteration occurring during LC separations places stringent demands on the LC method-ology, solvents and materials used, and procedures employed during work-up of fractions and their storage prior to testing. However, the simplicity and direct relevance of stability test results to the issue of fuel stability makes it the method of choice for evaluation of fractions. In contrast, detailed analysis of fresh versus aged fuel fractions proved to be a very laborious approach for estimating their stability (23). Thus, the prudent course of action is to improve separation and reblending techniques where necessary, rather than to look for alternate methods for fraction evaluation.

Although more difficult experimentally, work with actual fuel fractions provides a more realistic assessment of stability problems than possible with simple model systems.

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